

## **IMPROVED ECMP SYSTEM**

### **FIELD OF THE INVENTION**

**[0001]** This invention relates generally to electrochemical processing of materials and, more particularly, relates to an improved system for IR-correction within an electrochemical apparatus.

### **BACKGROUND**

**[0002]** A number of types of electrochemical cells are known and used in various capacities. A most basic electrochemical cell involves a working electrode and a counter electrode substantially immersed in an electrolytic solution. A potential difference applied between the working electrode and counter electrode stimulates or influences a cell reaction. Typically, the overall reaction in the cell is comprised of two half reactions taking place at the interfacial regions between the electrodes and the electrolytic solution. The reaction at the working electrode is generally the reaction of interest. Reactions of interest for example include reduction or oxidation.

**[0003]** Looking at the interfacial layers in greater detail, each such layer typically has associated with it a capacitance sometimes referred to as the double-layer capacitance. This capacitance is affected by the specifics of the applied potential, current, materials, reactions, and kinetics within the cell. Due in part to this capacitance effect, information about the cell behavior can be obtained by applying an electrical perturbation to the cell, such as via the applied potential or current, and observing the resultant cell behavior. For example, treating the cell as a series resistance and capacitance, an applied voltage step should result in an exponentially decaying measured current response. Likewise, an applied sustained current step should result in a substantially linearly increasing measured potential. From these

techniques, the interfacial properties, in particular the voltage across the interface, can be roughly inferred.

**[0004]** In systems where the solution resistance is relatively high such that the resultant potential drop (IR) (comprised of the product of the current and the solution resistance) is significant, an additional “reference” electrode is usually placed near the working electrode. This reduces the IR component of the measured potential and allows a more accurate measurement of the voltage at the interface of the working electrode and the solution. Even so, the use of a reference electrode in such a manner typically does not completely eliminate the error in the estimation of IR drop across the double layer. A number of feedback mechanisms have been employed in the prior art to roughly correct for the remaining IR contribution to some degree.

**[0005]** In electrochemical mechanical polishing (ECMP) techniques, the electrical potential at the interface between the working electrode and the electrolytic solution has a significant and often exponential impact on the material removal rate. Thus, to ensure uniform controlled removal of material, it is often of great importance to know and control the potential across the electrode-solution interface with high precision. However, existing IR correction techniques as discussed above do not allow such precise determinations or control and hence result in inferior control of the key process parameters for ECMP.

**[0006]** For these reasons and others, an improved IR correction system is needed that allows for precise control of the interfacial potential at the working electrode in an electrochemical cell.

### BRIEF SUMMARY OF THE INVENTION

[0007] Embodiments of the invention provide a new ECMP IR calculation and correction system that allows for the precise control of the interfacial voltage drop, and thus allows ECMP to be used for very precise surface polishing that would previously have been beyond the capabilities of ECMP. As used herein, the terms ECMP and electrochemical mechanical polishing refer to techniques for polishing, wherein the polishing effect is due at least in part to each of electrical, chemical, and mechanical actions.

[0008] The ECMP cell described herein may be a stand-alone cell or may comprise a module in an integrated processing system. Such integrated processing systems are made up of multiple individual process modules, matched to one another to ensure smooth manufacturing flow. Other process modules may provide, for example, deposition (metal, oxide, silicon), etching (metal, oxide, silicon), thermal processing (e.g., rapid thermal processing), ion implantation, other polishing, and inspection.

[0009] In greater detail, the ECMP system according to an embodiment of the invention comprises a working electrode, a counter electrode, and a reference electrode. A characteristic electrical perturbation is applied to the system and a unique IR calculation circuit is used to determine the IR drop due to portions of the system other than the interface of interest. Subsequently, in an embodiment of the invention, an IR correction is provided, whereby the interface voltage at the interface of interest is precisely controlled. As a result, the electrochemical polishing at the surface of interest is precisely controlled despite the IR drop in the system. It should

be noted that although ECMP is used as an exemplary process herein, the techniques described herein apply as well to electrochemical processes other than ECMP.

[0010] Additional features and advantages of the invention will be made apparent from the following detailed description of illustrative embodiments which proceeds with reference to the accompanying figures.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0011] While the appended claims set forth the features of the present invention with particularity, the invention, together with its objects and advantages, may be best understood from the following detailed description taken in conjunction with the accompanying drawings of which:

[0012] Figure 1 is a cross-sectional side view of a three-electrode electrochemical cell usable in implementing an embodiment of the invention;

[0013] Figure 2 is a is a schematic diagram of an electrical circuit modeling the cell of Figure 1;

[0014] Figure 3 is a schematic diagram of a current limiter device for use in an IR-corrected ECMP system according to an embodiment of the invention;

[0015] Figure 4 is a schematic diagram of an IR- corrected ECMP system according to an embodiment of the invention; and

[0016] Figure 5 is a flow chart showing steps taken to effect IR correction in an ECMP system according to an embodiment of the invention.

### DETAILED DESCRIPTION

In overview, in an embodiment of the invention, an essentially square step function voltage perturbation is applied to a potentiostat input to yield a decaying current spike at the potentiostat output. Subsequently, the current is limited by a current limiter so as to produce a substantially square step function current signal. The response of the ECMP cell to the applied current signal described above is observed, wherefrom the IR characteristics in the measured circuit are calculated. In an embodiment of the invention, an IR correction based on the calculated IR characteristics is derived and applied, so as to precisely control the potential across the interface of interest, such as at the working electrode. Note that the term “correction” as used herein does not require complete elimination of the unwanted IR component. Rather, the techniques described herein allow the IR component to be more precisely known in real-time, and allow control or correction substantially to a desired degree. In an embodiment of the invention, the voltage across the substantially capacitive interface between the working electrode and the electrolyte is controlled to within a small variance, such as about 10mV, of a predetermined target value.

[0017] Turning to the drawings, wherein like reference numerals refer to like elements, aspects of embodiments of the invention will be described in greater detail. Figure 1 illustrates in simplified cross-sectional side view a three-electrode electrochemical cell according to an embodiment of the invention. The cell 101 is comprised of a container 103, a counter electrode 105 and an electrical lead 107 associated with the counter electrode 105, a working electrode 109 and an electrical lead 111 associated with the working electrode 109, and a reference electrode 113. The counter electrode 105, working electrode 109, and reference electrode 113 are immersed in electrolyte 115.

**[0018]** In operation, a voltage is applied between the counter electrode 105 and the working electrode 109 via their respective leads 107, 111. The applied voltage is dropped across the interface of interest at the working electrode 109 as well as via various impedances. Note that, in one embodiment of the invention, the cell 101 also comprises a mechanical abrasion surface adjacent the working electrode surface of interest. For example, a polishing pad that undergoes rotational and/or lateral motions may be used to provide mechanical polishing of the surface as well.

**[0019]** An equivalent electrical circuit representation of the ECMP cell 101 is shown in the schematic diagram of Figure 2. In particular, the representative circuit 201 comprises a number of electrical elements, including resistive and capacitive elements, that together substantially model the behavior of the actual ECMP cell. In greater detail, the circuit model 201 represents the cell 101 as a combination of the electrical equivalences of the counter electrode 203, the reference electrode 205, and the working electrode 207, as well as the impedance interrelationships among the elements.

**[0020]** Each representation 203, 205, 207 comprises both resistive and capacitive impedances. For example, the model 203 of the counter electrode comprises a resistive impedance 209 in parallel with a capacitive impedance 211, with the entire model 203 being linked to the reference electrode model 205 via a series of resistive impedances 213 and 217, and to the working electrode model 207 via the sum of the resistive impedance 213 and a resistive impedance  $R_s$  (solution resistance) 215. The reference electrode model 205 comprises a parallel combination of a resistive impedance 219 and a capacitive impedance 221. The reference electrode model 205 is tied to the working electrode model 207 via the series of resistive impedances  $R_s$

215 and resistance 217. Finally, the working electrode model 207 comprises a resistive impedance 223 in parallel with a capacitive impedance 225. It should be noted that although the three inputs/outputs 227, 229, 231 of the overall cell model 201 represent the leads of the electrical elements of Figure 1, the respective component models 203, 205, 207, with their respective resistive and capacitive impedances, also encompass the electrical characteristics of the respective leads as well in an embodiment of the invention.

[0021] It can be seen that the effective circuit between the reference electrode 113 and the working electrode 109 comprises the resistance 223 and capacitance 225 of the interfacial layer of interest as well as an essentially unavoidable series resistance contribution  $R_s$  from the electrolyte itself. In order to accurately control the interfacial voltage drop, it is important that the contribution  $R_s$  be determined and corrected for. In particular, a current  $I$  passing through the electrolyte in the region between the reference electrode 113 and the working electrode 109 will cause a voltage drop of  $IR_s$  from the voltage  $V_{ref}$  measured at the reference electrode 113. In other words, the voltage across the interface of interest will be  $V_{ref} - IR_s$ .

[0022] As will be seen, the aforementioned model of the ECMP cell can be used to determine the value of  $R_s$  215. In particular, if an essentially square step function perturbation (voltage or current) is input to the cell via lead 107, represented by 227 in the model 201, the response of the ECMP cell can be predicted.

[0023] Initially, it is noted that for a general linear differential equation of the first order in  $y$ , where  $P$  and  $Q$  are functions of  $x$  alone, or constants,

$$\frac{dy}{dx} + Py = Q \quad (1)$$

the general solution is

$$y = e^{-\int P dx} \left( \int Q e^{\int P dx} dx + K \right) \quad (2)$$

[0024] For the case of a constant current (magnitude  $I_p$ ) square step function (e.g., the initial portion of the perturbation is made up of contiguous substantially linear segments of differing slopes, one having zero slope, regardless of the shape of the latter portion of the perturbation) through a parallel connection of a resistance  $R_p$  and a capacitance  $C$ , where  $V$  is the voltage across the parallel combination,  $R_p C$ , and neglecting for the moment  $R_s$ ,

$$\frac{dV}{dt} = \left( I_p - \frac{V}{R_p} \right) \frac{1}{C}; \frac{dV}{dt} + \frac{V}{R_p C} = \frac{I_p}{C}; \text{let } V = y; t = x; P = \frac{1}{R_p C}; Q = \frac{I_p}{C} \quad (3)$$

$$V = e^{-\int \frac{dt}{R_p C}} \left( \int \frac{I_p}{C} e^{\int \frac{dt}{R_p C}} dt + K \right) = e^{-\int \frac{dt}{R_p C}} \left( \frac{I_p}{C} \int e^{\int \frac{dt}{R_p C}} dt \right) + K e^{-\int \frac{dt}{R_p C}} \quad (4)$$

$$V = e^{-\frac{t}{R_p C}} \left( \frac{I_p}{C} \int e^{\frac{t}{R_p C}} \right) + K e^{-\frac{t}{R_p C}} = e^{-\frac{t}{R_p C}} \left( \frac{I_p}{C} R_p C e^{\frac{t}{R_p C}} \right) + K e^{-\frac{t}{R_p C}} \quad (5)$$

$$V = I_p R_p + K e^{-\frac{t}{R_p C}}; \text{when } t = 0, K = V_0 - I_p R_p \quad (6)$$

and the voltage  $V$  is the known exponential decay form

$$V = I_p R_p + (-I_p R_p) e^{-\frac{t}{R_p C}} = I_p R_p \left( 1 - e^{-\frac{t}{R_p C}} \right) \quad (7)$$

[0025] If, as in our model, there is also a simple resistor  $R_s$ , in series with this combination, curve (7) has an additional term  $I_p R_s$ .

$$V = I_p R_p \left( 1 - e^{-\frac{t}{R_p C}} \right) + I_p R_s \quad (8)$$

$$\text{Since } e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \quad (9)$$

For small  $t$ , (8) becomes

$$V = I_p R_p \left( 1 - 1 + \left( \frac{t}{R_p C} \right) - \frac{t^2}{R_p^2 C^2} \right) + I_p R_s = I_p \left( \frac{t}{C} - \frac{t^2}{R_p C^2} + \dots \right) + I_p R_s \quad (10)$$

Thus, when  $t \equiv 0$ ,  $V = I_p R_s$



[0026] The above analysis could be done by observation, such as on an oscilloscope, or by measuring the transient voltage at two points and extrapolating (computing) linearly back to zero time, or by quadratic extrapolation, using equations (21) - (23).

[0027] However, for fast rise time square step functions, any stray inductances add “spikes” in short time to the measured values, which obscure the transition times. Also note that with a slow rise time, the proper time to extrapolate back to is not  $t = 0$ . To find the correct time for a “slow” waveform, assume that the form of the current waveform during the switching time is a linear ramp, such that  $I = I_p t$ . This is a reasonable assumption for a first order amplifier like that in a typical potentiostat for the beginning of the waveform, and also for the end if the current is clamped at the top by suitable circuitry. For this linear ramp, the current  $I$  through the capacitor is equal to the total current less the portion going through the parallel resistor,  $V/R_p$ , where  $V$  is the voltage that has already developed across the capacitor at a time  $> 0$ . The resulting differential equation is:

$$\frac{dV}{dt} - \left( I_p - \frac{V}{R_p} \right) \frac{t}{C} = 0; \frac{dV}{dt} + \frac{t}{R_p C} V = \frac{I_p}{C} t; \text{let } V = y; t = x; P = \frac{t}{R_p C}; Q = \frac{I_p}{C} t \quad (11)$$

$$V = e^{-\int \frac{t}{R_p C} dt} \left( \frac{I_p}{C} t e^{\int \frac{t}{R_p C} dt} + K \right) \quad (12)$$

$$\int \frac{t}{R_p C} dt = \frac{t^2}{2 R_p C}; \int x e^{ax^2} dx = \frac{e^{ax^2}}{2a} \quad (13)$$

$$V = e^{-\frac{t^2}{2 R_p C}} \left( \int \frac{I_p}{C} t e^{\frac{t^2}{2 R_p C}} dt + K \right) = e^{-\frac{t^2}{2 R_p C}} \left( \frac{I_p}{C} \int t e^{\frac{t^2}{2 R_p C}} dt \right) + K e^{-\frac{t^2}{2 R_p C}} = R_p C \frac{I_p}{C} + K e^{-\frac{t^2}{2 R_p C}} \quad (14)$$

$$V = R_p I_p + K e^{-\frac{t^2}{2 R_p C}}; \text{ when } t=0 \ K=V_0 - R_p I_p; \text{ letting } V_0 = 0 \quad (15)$$

$$V = R_p I_p \left( 1 - e^{-\frac{t^2}{2 R_p C}} \right) \quad (16)$$

$$\text{Since } e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots \text{ and } e^{x^2} = 1 + x^2 + \frac{x^4}{2!} + \dots \quad (17)$$

$$V = R_P I_P \left( -x^2 - \frac{x^4}{2!} + \dots \right) = R_P I_P \left( \frac{t^2}{2R_P C} + \frac{t^4}{8R_P^2 C^2} + \dots \right) = \frac{I_P t^2}{2C} + \frac{I_P t^4}{8R_P C^2} + \dots \quad (18)$$

or for large  $R_P$  or small  $t$ , integrating directly from

$$\frac{dV}{dt} = I_P \frac{t}{C} \quad (19)$$

$$V = \frac{I_P}{2} \frac{t^2}{C} \quad (20)$$

[0028] Thus, for a linear ramp of the current to the final value, the voltage,  $V$ , grows quadratically, and the proper time for extrapolation is at the halfway point of the ramp. The equations for finding the parabola with which to extrapolate are given by equations (21) - (23), assuming for the sake of example that the voltage  $V$  is measured at three times ( $t(1)$ ,  $t(2)$ ,  $t(3)$ ) to yield three measurements ( $V(1)$ ,  $V(2)$ ,  $V(3)$ ).

$$V(n) = at(n)^2 + bt(n) + c; \quad (n = 1, 2, 3) \quad (21)$$

$$D = \begin{vmatrix} t(1)^2 & t(1) & 1 \\ t(2)^2 & t(2) & 1 \\ t(3)^2 & t(3) & 1 \end{vmatrix} \quad (22)$$

$$a = \frac{\begin{vmatrix} V(1) & t(1) & 1 \\ V(2) & t(2) & 1 \\ V(3) & t(3) & 1 \end{vmatrix}}{D}; \quad b = \frac{\begin{vmatrix} t(1)^2 & V(1) & 1 \\ t(2)^2 & V(2) & 1 \\ t(3)^2 & V(3) & 1 \end{vmatrix}}{D}; \quad c = \frac{\begin{vmatrix} t(1)^2 & t(1) & V(1) \\ t(2)^2 & t(2) & V(2) \\ t(3)^2 & t(3) & V(3) \end{vmatrix}}{D} \quad (23)$$

[0029] A new and useful current limiter usable to clamp a potentiostat output to create a current step function as discussed above is shown in Figure 3. In particular, the illustrated circuit 301 is a modification of an AC current switch. When the circuit 301 is used as a switch, resistor 303 and resistor 305 are of zero resistance, and the photovoltaic isolator 307 is either turned fully on or fully off. Typically the resistance 310 is about 1Mohm to allow the voltage at node 313 to decay when the applied voltage across terminals 309, 311 is turned off.

[0030] In order to use the circuit 301 as a current limiter, the externally applied voltage across terminals 309, 311 is made externally adjustable. Exemplary input devices for supplying a variable voltage include any number of resistive and solid-state devices as will be appreciated by those of skill in the art. In an embodiment of the invention, the input across terminals 309 and 311 is supplied by a commercial adjustable potentiostat. In addition, the use of resistors 303 and 305 makes the maximum current that can flow through the circuit (between terminals 319 and 321) externally controllable in real time. The choice of resistors depends upon the range of currents that will be passed by the circuit 301, consistent with minimizing power dissipation and overall voltage drop between terminals 319 and 321. For example, if the maximum current is to be  $\pm 2A$ , the resistors 303 and 305 can be 5-Watt resistors of approximately 1 ohm. Alternatively, if the maximum current is to be  $\pm 20A$ , the resistors 303 and 305 can be 20-Watt resistors of approximately 0.1 ohm or 10-Watt resistors of approximately 0.05 ohm. In order to use the novel current limiter 301 in the ECMP circuit, the circuit 301 is placed, by terminals 319 and 321, in series between the output of the potentiostat and the lead of the counter electrode.

[0031] An exemplary system used to correct for  $IR_s$  according to the principles described above is shown in Figure 4. The system 401 comprises a potentiostat 403, and an ECMP cell 405. To reiterate, as with the cell of Figure 1, the cell 405 comprises a counter electrode 407, a working electrode 409, and a reference electrode 411. The reaction of interest is the one at the surface of the working electrode 409, and thus the voltage of interest is the voltage across the interfacial layer of that electrode 409 in operation. The reference electrode 411 measures this voltage supplemented by the voltage  $IR_s$ .

[0032] In addition to the aforementioned elements, the system 401 also comprises a current limiter 413, whose design may be as described above with reference to Figure 3. The current limiter 413 is placed in series between the output of the potentiostat 403 and the lead of the counter electrode 407, and acts to current limit the output of the potentiostat 403. Note that in an embodiment of the invention, a current measurement device 415 is placed in series between the current limiter 413 and the lead of the counter electrode 407.

[0033] The reference electrode 411 is connected, through a buffer, to the positive input of a differential amplifier 417 via resistor 434, and the working electrode is connected, also through a buffer, to the negative input of the differential amplifier 417 via resistor 435. Thus the output 419 of the differential amplifier 417 represents the voltage difference between the reference electrode 411 and the working electrode 409 (note that as will be discussed below the differential amplifier inputs are altered slightly during IR correction). This voltage initially represents both the voltage of interest and an  $IR_s$  contribution. The output 419 of the differential amplifier 417 is input to an analog-to-digital converter 421, which operates to produce a digital output 423.

[0034] The digital output 423, which still represents the voltage difference between the reference electrode 411 and the working electrode 409 as modified, is fed to a computing device 425 such as a computer for calculation of the  $IR_s$  contribution to the measured voltage according to the principles discussed above. The computer 425 generates a digital correction factor by which to multiply the measured current in order to minimize the  $IR_s$  contribution in the measured voltage. The digital correction factor is output on line 427 to a digital-to-analog converter 429 to produce an analog

correction factor. In turn, the analog correction factor is input to an analog multiplier 431, which outputs a representation of the product of the measured current from current measurement device 415 and the analog correction factor. This output is used as one end of a voltage divider formed of resistors 433 and 435, the other end of which is the measured voltage of the working electrode 409. Thus, an IR factor is combined into the working electrode voltage at the input to differential amplifier 417. This feedback is used by computer 425 to minimize the IR contribution in the measured signal.

[0035] Moreover, note that differential amplifier 417, multiplier 431, and digital-to-analog converter 429, as well as their respective inputs and outputs, are mirrored in differential amplifier 437, multiplier 439, and digital-to-analog converter 441. However, instead of being fed to the analog-to-digital converter 421, the output of differential amplifier 437 provides an input to the potentiostat 403 to control the output thereof. Thus, differential amplifier 417, multiplier 431, and digital-to-analog converter 429 are used by the computer 425 to calculate an IR correction through feedback while differential amplifier 437, multiplier 439, and digital-to-analog converter 441 are used to apply the correction to the actual circuit by controlling the potentiostat. The end result is that the  $IR_s$  contribution is known, and the cell voltage is controlled such that the voltage between the reference electrode 411 and the working electrode 409, minus the  $IR_s$  contribution, is maintained at the desired value.

[0036] An exemplary process for using the aforementioned elements to effect the desired IR correction is described in greater detail with respect to the flow chart 500 of Figure 5. Initially, a small square step function voltage perturbation is applied to the input of the potentiostat 403 at step 501. Many techniques can be used to apply

this perturbation to the potentiostat input, but in an embodiment of the invention, the computer 425 manipulates the input to the digital-to-analog converter 441 (and hence also digital-to-analog converter 429) to produce the desired perturbation. The result of the application of the small square step function perturbation to the potentiostat input is that exponentially decaying current spikes are superimposed on the prior potentiostat output.

[0037] At step 503, the current limiter 413 clips the current to a predefined maximum level. This level may be set by several means; however, in the embodiment of the invention shown in Figure 3, the limitation is established via the voltage placed across the control terminals 309, 311. This clipping results in the formation of a substantially square step function in the current supplied to the ECMP cell. As noted above, the term substantially square implies a waveform that is substantially square in its initial rise (or fall), whether the waveform appears substantially square overall.

[0038] At step 505, the current through the ECMP cell as well as the voltage between the reference electrode and the working electrode are measured at about the time of the applied perturbation. In an embodiment of the invention, these measurements are as follows: the voltage is measured at three times just before the step and at three times just after; current is measured at the same times or at a subset of those times; and both quantities are measured with greater frequency during the transient behavior of the cell to determine the rise time of the waveform. Alternatively, measurements are taken with uniform temporal frequency in an embodiment of the invention. Note that the measurements may be by human intervention, but are more practically computer-executed for the sake of speed, accuracy, and convenience.

[0039] At step 507, the equations set forth above for predicted cell behavior are solved using the gathered data from step 505. In addition to the mathematical calculations described above, this step may also involve optimization via a feedback loop as described with reference to Figure 4. In this manner, the  $IR_s$  component between the reference electrode and the working electrode is calculated.

[0040] Finally, the IR correction is applied to the cell in step 509 so that the measured voltage minus the IR component is equal to the desired interfacial voltage. In this manner, the interfacial voltage, and hence the polishing effect at the interface, is accurately controlled. Note that the manner in which the IR correction is accomplished is not critical. In an embodiment of the invention, a fraction, such as  $2/3$ , of the correction is applied to digital-to-analog converter 441 for IR correction.

[0041] It will be appreciated that an improved IR correction method and system have been described herein. In view of the many possible embodiments to which the principles of this invention may be applied, it should be recognized that the embodiments described herein with respect to the drawing figures are meant to be illustrative only and should not be taken as limiting the scope of invention. For example, although the examples herein focus primarily on the application of the invention to ECMP, it will be appreciated that the described techniques apply as well to other types of electrochemical cells and the use thereof. Therefore, the invention as described herein contemplates all such embodiments as may come within the scope of the following claims and equivalents thereof.